

Soot Particle Formation in Diffusion Flames

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I. Introduction

Over the past twenty five years a large number of investigations of soot formation, growth and oxidation have been reported. The extensive interest in this problem is a result of the important ramifications that the presence of soot particles have on practical combustion systems. Because of the diversity of these effects, a wide variety of experimental situations have been investigated. These range from small laboratory scale burners to full scale combustion devices. However, insights into the fundamental processes which control the formation and growth of soot particles have largely resulted from studies of simple premixed and diffusion flames. The results of such studies have been periodically reviewed and where applicable related to practical situations [1-4].

Recently a significant amount of attention has been given to the study of laminar and turbulent diffusion flames [5-15]. Many of these studies have utilized optical diagnostics to obtain quantitative information on soot particle size, concentration and spatial distribution in the flame. These techniques which were first applied to premixed flames [16] have allowed for a significant advance in our quantitative understanding of soot formation processes. In fact, the results of the premixed flames studies established the common sequence of events which is now viewed to govern the formation of soot particles in most combustion situations. These include (1) a chemically kinetically controlled reaction sequence which results in the formation of precursor species needed to form the first particles, (2) a particle inception stage which results in the formation of large numbers of small primary particles, (3) a particle growth period in which surface growth and particle coagulation processes contribute to the increase in particle size and (4) a stage in which material is no longer added to the soot particles and size is controlled by agglomeration or may even be reduced by oxidative attack. Recent work in premixed flames has concentrated on more firmly establishing quantitative measurements of the individual processes which constitute this description. Significant progress has been made in understanding the surface growth and particle coagulation processes which occur in premixed flames [17,18]. Results from these and other studies have emphasized the importance of acetylene (C_2H_2) and available surface area in the particle growth process and have established that soot particle coagulation accounts for the particle number concentration behavior observed in such flames. Presently efforts are focused on the particle inception stage in an effort to link the formation of large intermediate hydrocarbon species which are viewed as precursors to soot

particles and the initial particles observed by light scattering techniques in the flame [19,20]. Such measurements present serious challenges for current diagnostic approaches and progress has been possible only through a combination of experimental measurements and extensive computer modelling of the soot aerosol as it develops in time. In these studies, the effects of particle inception, surface growth and coagulation must be taken into account simultaneously.

Recent studies in laminar diffusion flames have essentially confirmed that the formation and growth of soot particles can be described by a similar series of processes. Using laser-based techniques to measure particle size [6,7], velocity [9,10] and temperature [21], workers have provided a much more detailed understanding of soot particle processes in these flames. Because particle formation is not spatially homogeneous throughout the flame, the high spatial resolution of these techniques have allowed investigation of the structure of the soot particle field and, at least to some degree of accuracy, to follow the time history of the particles as they proceed through the flame [10,11,22]. In particular, attention has been given to the study of effects of temperature [23,24] and pressure [22] on the production of soot particles. Of related interest are studies examining radiative transfer from these flames which indicate that radiation from soot particles represents a significant energy transfer mechanism [15]. This has led several workers to speculate that radiative transfer is important in controlling the emission of soot particles from the flame [7,11,15].

In addition to these studies, which have emphasized the detailed processes involved in soot particle and growth, a large body of work exists concerning the relative sooting tendency of fuels [12,25,26]. These works largely focus on the concept of a "smoke point" or "sooting height" which characterizes an individual fuel. The sooting height is an experimental measurement of the height of a laminar diffusion flame when soot particles are observed to issue from the tip of the flame. Fuels which have a higher tendency to soot are found to have a shorter flame height at this characteristic point. Although a qualitative measure of soot production tendencies, workers investigating soot formation from this approach have made several critical contributions to the phenomenological understanding of soot particle formation [27]. Recently work has appeared to relate the more detailed measurement results in laminar and turbulent flames to these sooting height results with some success [28,29]. This work is particularly significant in that it allows a quantitative relationship to be obtained from the previous relational information on a wide variety of fuels. The fact that information for turbulent flames could be derived from laminar flame measurements is encouraging since it points to the general utility of the laminar diffusion flame results.

It should be mentioned that a good deal of the understanding of the evolution of the soot particle field in diffusion flames draws substantially from the earlier work of Roper [30,31]. In these papers, and recently in an update to that work [32], a simple model of laminar diffusion flames is developed which clearly describes the effects of fuel flowrate, temperature and radiation on the structure of the flame. These works have widely influenced other researchers in this field.

In the above work on diffusion flames, the emphasis has been on the particle aspects of these flames. Studies of the important chemistry have been undertaken for the most part in low pressure and atmospheric laminar premixed flames, although shock tube work has also contributed in some respects [33,34]. These studies have established plausible reaction mechanisms leading to the formation of aromatic compounds with a few rings. There continues to be a debate concerning the role that ions may have in providing the rapid chemical reaction rates needed to form the particles in the reaction times available (~ 1 ms) [35]. However, in the area of diffusion flames a relatively smaller amount of work is available examining the preparticle chemistry [36]. Recently a significant effort has been made to study both the chemistry leading to soot precursors and the subsequent soot particle growth in diffusion flame environments [9]. These results have not yet progressed sufficiently to allow a complete quantitative picture to be drawn, but progress is continuing [37].

The experiments to be described here are an extension of our previous laminar diffusion flame studies of soot particle formation [7,10]. Specifically a detailed examination of the effect of fuel chemical structure has been undertaken. In our previous work, the emphasis has been on examining the effects of fuel flowrate and temperature on the production of soot in diffusion flames [7,10,24]. In addition, specific attention was given to the processes controlling the emission of soot particles from the flame. These results along with the findings of other researchers has established the complex, coupled nature of the processes determining the soot particle evolution in the flame. The individual effects of temperature, flow field (e.g. velocity), pressure and fuel constituents all must be investigated if a comprehensive understanding of the soot formation process is to be achieved.

II. Experimental Apparatus

For these studies, a coannular laminar diffusion flame has been used in which fuel is burned in air under atmospheric pressure conditions [7]. The burner consists of an 11.1 mm id fuel passage surrounded by 101.6 mm outer air passage. The flame is enclosed in a 405 mm long brass cylinder to shield the flame from laboratory air currents. Slots machined in the chimney provide for optical access while screens and a flow restrictor were placed at the exhaust of the chimney to achieve a stable flame. The burner is mounted on translating stages to provide three-dimensional positioning capability. Radial traversing of the burner is accomplished using a motorized translation stage.

The soot particle measurements were obtained using a laser scattering/extinction technique [16]. Laser extinction and scattering measurements were carried out using a 4 W argon ion laser which was operated at the 514.5 nm laser line. The incident laser power was 0.5 W and was modulated using a mechanical chopper. The transmitted power was measured using a photodiode and the scattered light was detected at 90° with respect to the incident beam using a photomultiplier tube. Signals from each detector were input to a lock-in amplifier and subsequently digitized signals were stored on a computer. The ratio of the measured scattering cross section to the extinction coefficient was used to determine particle size. For these calculations, the particle size

analysis was carried out using a data reduction approach based on Mie theory.

Previously obtained velocity measurements on a similar flame, obtained using a laser velocimeter technique, were used to calculate the particle paths and the residence time in the flame.

III. Results

As has been previously described, the amount of soot formed in a flame is a function of several variables. Temperature, pressure and fuel structure have been shown to be particularly important in determining the amount of soot formed. Thus, it is highly desirable to study soot particle formation under conditions where these variables can be systematically varied. This presents several problems, particularly in the case of fuel structure studies, because the sooting propensity of fuels varies widely [25-27]. This results in important variations in the velocity field and heat losses to the burner for different flames.

To overcome some of these difficulties, a fuel mixture approach has recently been tried for the study of soot particle processes in these flames. In this approach, an ethene/air diffusion flame which has been extensively characterized in terms of the particle, velocity and temperature fields has served as the baseline flame [7]. For the fuel composition studies, different fuel species were added to the baseline fuel (ethene), such that the additional carbon flow rate was the same in each case. Under these conditions, the total carbon flow rate is held constant. In addition, the flame size and shape remains similar for all the flames studied, thus minimizing changes in burner heat loss or particle transport in the flame. An ethene fuel flow rate of 3.85 cc/s (a carbon flow rate of 3.78×10^{-3} gm/s) was selected for the baseline flame since this diffusion flame has been extensively studied [7,10,22]. A second fuel was added to the ethene flow to produce a total carbon flow rate of 4.81×10^{-3} gm/s, an increase of 1.03×10^{-3} gm/s from the baseline case. Results have been obtained for methane, ethane, ethene, acetylene, propene, butene, and toluene. In the case of toluene, the fuel was vaporized using a technique similar to that described by Gomez et al. [12]. The flow conditions for these studies are given in Table 1 along with the calculated adiabatic flame temperatures for the fuel mixtures. Table 1 also includes the measured values for the percent carbon conversion to soot for the fuel increment introduced into the baseline flame. This value is obtained by taking the difference between the maximum soot mass flow rate observed in the flame for the fuel mixture case and the baseline flame divided by the carbon mass flow rate increase (1.03×10^{-3} gm/s). The percent conversion is observed to vary strongly as a function of fuel species with the aromatic fuel having the largest conversion percentage.

Using the previously obtained detailed information on the particle paths for the ethene flame, comparisons between the different fuels can be made for different regions of the flame. Two regions of the flame have been selected for illustration using the soot volume fraction (f_v) measurements. Figure 1 shows the time evolution of f_v along the particle path which traverses the annular region of the flame where the maximum f_v

Table 1

Baseline Fuel	Fuel Added	T _{ad}	Carbon Conversion
(cc/s)	(cc/s)	(K)	(%)
C ₂ H ₄ (3.85)	+ CH ₄ (2.10)	2333	13
"	+ C ₂ H ₆ (1.05)	2344	22
"	+ C ₂ H ₄ (1.05)	2369	18
"	+ C ₂ H ₂ (1.05)	2403	32
"	+ C ₃ H ₆ (0.70)	2368	36
"	+ C ₄ H ₈ (0.525)	2359	52
"	+ C ₇ H ₈ (0.30)	2361	98

is observed; Figure 2 shows a similar plot for the center line of the flame. The fuel mixtures shown include three alkenes (ethene, propene and butene) and an aromatic (toluene). As Table 1 indicates, the adiabatic flame temperatures for these fuel mixtures do not vary significantly. Thus, the temperature fields characterizing these flames should be similar, allowing a direct comparison between the flames.

Figures 1 and 2 clearly indicate that differences between the fuels are more pronounced in the annular region of the flame than near the center line. This implies that the higher temperatures and larger radical concentrations present in the annular region of the flame, which lies closer to the flame reaction zone, not only increase the soot formation rates, but also enhance the differences between fuel species. In the annular region (see Fig. 1), all the fuels are observed to reach a maximum in f_v at a similar residence time (≈ 60 ms). For the alkene fuels, the observed residence time for the first observation of soot particles and the value of f_v at this time are also very similar. However, the different alkene fuels are observed to have measurably different rates of growth in terms of the change in the soot volume fraction with time. For the toluene mixture, although soot particles are first observed at a similar residence time (≈ 21 ms), the initial concentration is much higher. This implies that soot particle inception occurred at an earlier time or that the inception process is much more vigorous. The particle size and number density measurements, along with the results from nearby particle paths, favor an interpretation indicating an earlier inception time. Thus, these results indicate that the specific nature of the fuel species is observed to affect the initial particle formation process as well as the subsequent growth rates. Comparisons with the data along the center line of the flame (see Figure 2) further support the argument that the aromatic fuel accelerates the inception process. However, the final soot volume fraction values observed in this region show smaller differences as compared to the annular region of the flame for the fuels studied. Thus, the particle growth processes may differ in this fuel rich region which also exhibits lower temperatures than observed in the annular region.

The approach of determining the influence of fuel structure based on fixed increments in the carbon flow rate provides an appropriate framework in which to consider the soot formation process in general. As an example, Fig. 3 shows a plot of the maximum soot mass flow rate as a function of fuel flow rate for a series of ethene/air flames [7,10]. A linear relationship is observed over the flow range studied, indicating that the conversion of fuel carbon to soot is constant beyond some minimum required flow rate to first produce soot particles in the flame. The observed value for the percent conversion for these ethene flames is 18%. Similar experiments for other fuels are presently underway.

IV. Discussion

The results described above, although preliminary nature, have identified several features which are deserving of further investigation. Attention should be focused on differentiating the particle inception and surface growth contributions for the various fuel types. The differences between the alkene and aromatic fuels is, obviously, of most interest in light of the large differences in their sooting tendencies. In addition, the occurrence of a constant conversion percentage based on fuel structure needs further investigation. Specifically, this relationship for fuel mixtures needs to be developed over a wider variation of fuel structures and as a function of temperature. Recently, Kent [28] has reported soot conversion percentages for a wide variety of fuels which were directly related to soot volume fraction measurements obtained at the sooting height [28,38]. In this case, the conversion percentages are based on the total amount of conversion of fuel to soot rather than on the incremental change as described above. However, the trends observed in terms of the contrast between the alkene and aromatic fuel species are similar to those observed here. Kent's results indicate the conversion percentage for ethene to be 12% while that for toluene is 38%. The values for acetylene and propene were 23% and 16% respectively which differs in the ordering observed in the present study. However, the present results agree with previous studies of sooting height measurements in terms of the sooting tendency of the studied fuels [12]. These results along with the previous studies mentioned represent the beginning steps to obtaining a quantitative understanding of the effect of fuel molecular structure on soot formation in diffusion flames. Significant progress is likely to continue as experimenters concentrate on specific aspects of the problems such particle inception and surface growth.

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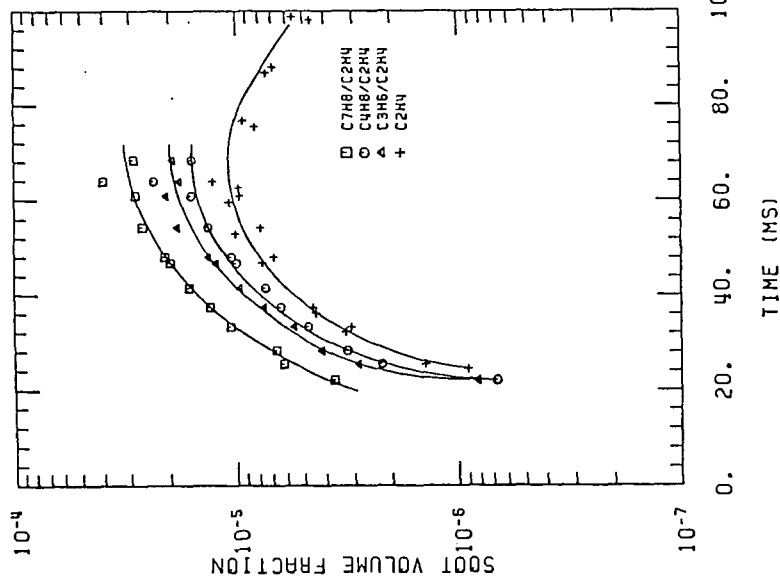


Figure 1. Comparison of the soot volume fraction, along the streak line exhibiting the maximum soot volume fraction for fuel mixtures containing ethene, propene, butene or toluene.

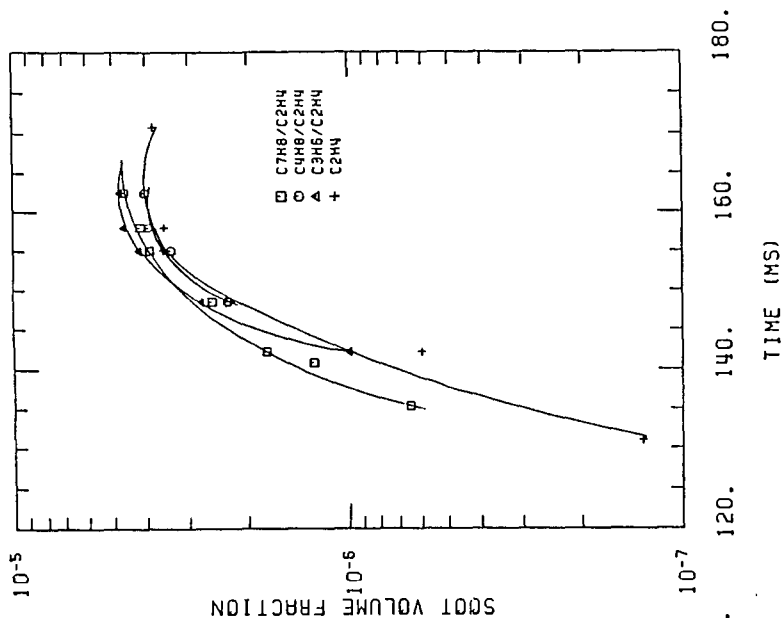


Figure 2. Comparison of the soot volume fraction along the center line of the flame for fuel mixtures containing ethene, propene, butene or toluene.

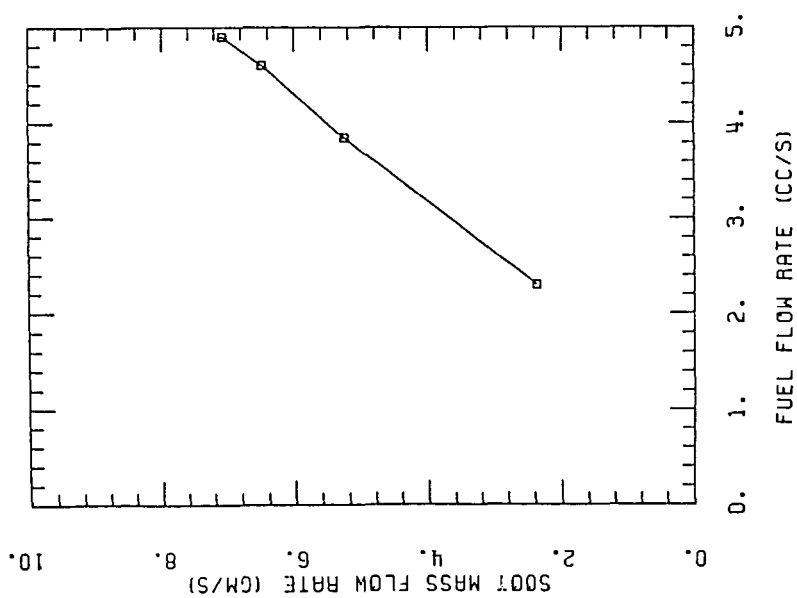


Figure 3. The maximum soot mass flow rate as a function of fuel flow rate for an ethene air diffusion flame.